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TITLE: LASER-INDUCED BREAKDOWN SPECTROSCOPY: DETECTING SODIUM AND POTASSIUM IN COAL GASIFIERS

AUTHOR(S): T.R. Loree and L.J. Radziemski

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University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545
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LASER-INDUCED BREAKDOWN SPECTROSCOPY:

DETECTING SODIUM AND POTASSIUM IN COAL GASIFIERS

T. R. Loree and L. J. Radziemski

University of California
Los Alamos National Laboratory
P. O. Box 1663
Los Alamos, New Mexico 87545

I. INTRODUCTION

One of the classic techniques for the detection of atomic species is the analysis of optical spectra emitted from an excited sample. In general, emission spectroscopy requires a method of exciting the medium of interest, a light gathering system, a spectral resolver, and a photon detector. We are investigating a variant of emission spectroscopy called LIBS, an acronym for laser-induced breakdown spectroscopy. While conventional in the detection methods, this approach excites the sample materials by the breakdown that occurs in the focal spot of a high-powered laser beam.

The breakdown generates a plasma[1] of excited atoms, ions (singly-ionized under our conditions), and electrons, all of which radiate brightly. The laser pulse is quite short (tens of nanoseconds) but the plasma lasts for tens of microseconds. The initiation of the breakdown requires a reasonable mass of material in the focal volume; that mass can be in the form of a gas, entrained particles in a gas, or a solid surface. For studies of coal gasification we are concerned with mixtures of gaseous compounds and entrained ash particles. Whatever the composition of the parent medium, the plasma contains only the constituent atomic species, with molecules and radicals appearing in recombination as the plasma cools.

II. LIBS EXPERIMENTS

Since the LIBS technique requires only optical access, and not physical intrusion, it is well suited to sampling hostile environments. A representative apparatus is shown in Fig. 1, a schematic of the setup used in our gasifier field tests. The laser beam enters from the left, is focused into the product stream, and causes breakdown there. The emitted light is gathered

from a viewing port, dispersed by a spectrometer, and detected and recorded by an optical multichannel analyzer. An analysis of the recorded spectra then identifies the atomic makeup of the product gas. Both detection and analysis can be carried out at various levels of complexity, to the limits of one's finances and time. In our gasifier tests, we limited our efforts to the degree required t .. ect and unambiguously identify sodium and potassium. Detailed information pertinent to Fig. 1 is contained in Appendix A.

The coal gasifier/combuster used in the field tests was a laboratory-scale device built under the leadership of Prof. Paul Hedman in the Chemical Engineering Department of Brigham Young University. The conditions in the test section are detailed in Appendix B. The field testing was preceded by six months of intensive experimentation, establishing the necessary background information on gases and particulate spectra, including samples of powdered BYU coal.

An example of the survey spectra obtained from the gasifier is given in Fig. 2. The dominant spectral line is the hydrogen alpha at 656.3 nm. The next strongest spectral line comes from oxygen, followed by characteristic lines of sodium and potassium. The identifications were not made from these rough spectra; in Figs. 3 and 4 we show the medium-resolution spectra in the regions of the sodium and potassium lines, along with calibration lines from a standard neon lamp. The sodium doublet was further pursued to higher resolutions, where the observed splitting confirmed identification.

We thus achieved the goals of the field testing, which was to simply detect sodium and potassium in the field, and in real time These spectra required 25 seconds of collection time (256 laser shots) for valid statistics, but the spectral lines were observable in a single shot. Since there is some line broadening and an increase in white light at higher pressures, it was to

our advantage that the gasifier was running at atmospheric pressure. These problems, however, may be ameliorated by an extension of the LIBS technique, called TRELIBS (for time-resolved LIBS).

III. TRELIBS DEVELOPMENT

Subsequent to the LIBS field test, we tried adding time resolution to the detector section. This was done by using either a time-gated optical multichannel analyzer, or gating the signal from a photomultiplier. In the latter case, the spectral resolver was either a scanning monochromator or a narrowband transmission filter.

It was immediate! clear that with LIBS we had been integrating quite a bit of optical history, which with TRELIBS was resolvable into its various components. This is shown in Fig. 5, a series of TRELIBS spectra for a sample of oxygen at STP conditions. The spectra are not corrected for the wavelength sensitivity of the diode array, and thus are relative, but it is clear that the early spectra contain ionic lines superimposed on a strong continuum, while the late-time spectra contain only neutral atomic lines, with very little background. The improved signal-to-noise and detectability at late times were unintentionally demonstrated in this example by the appearance of hydrogen lines from an unsuspected impurity in the oxygen sample.

As the strongest sodium and potassium spectral lines (Figs. 3 and 4) are neutral atom emissions, one should gain in detectability for these elements by going to late-time TRELIBS. This is illustrated in Fig. 6, which contrasts early and late-time spectra from NaCl in air. The early spectrum is essentially that of air, with no detectable sodium emission from the NaCl particles. In the late spectrum, however, the sodium D lines dominate the air contribution, and the white light background is negligible.

TRELIBS is also of use in avoiding the line-broadening effects that can be seen in LIBS spectra at high pressures. This is shown in Fig. 7, which compares LIBS spectra of 1 and 10-atm helium and a delayed 10-atm TRELIBS spectrum. The delayed spectrum is, as expected, composed only of sharp neutral lines; the delay time required to develop these is shorter than at 1 atm.

We are engaged in an effort to obtain absolute calibrations that will enable us to derive sample concentrations from observed signal amplitudes. The apparatus being used in the first round of testing is shown in Fig. 8. A known solution of NaCl is aspirated by a nebulizer into a known gas flow. This is heated before passing into the experimental optical cell, so that the laser focus takes place in a region of known NaCl concentration. From the focal volume, one can derive the actual mass of sodium being sampled. Figure 9 shows the sodium doublet observed with 85 pg in the plasma on each shot, taken after a delay of 5 μs. In this case the detection system consisted of a 1/2-m scanning monochromator and a photomultiplier. From the signal-to-noise ratio of this trace, one would estimate that one could detect 20 pg (2 mg/m^3) of sodium with this particular apparatus. This is by no means intended to represent a limit of detectability for sodium by TRELIBS, since the apparatus under discussion is far from an optimum embodiment. Using a narrow-band transmission filter and photomultiplier detection system (instead of the more general monochromator/photomultiplier) would allow collection of several orders of magnitude more signal. The present focal volume can also be increased, which for a fixed detectable mass would increase the concentration sensitivity. The critical issue will be the influence of such changes on the signal-to-noise ratio.

IV. CONCLUSIONS

The goal of this research program is the eventual development of a real-time monitor of trace quantities of elements present in hostile environments such as coal gasifier process streams. With LIBS, we have demonstrated the ability to probe a real process stream and achieve appropriate levels of detectability for sodium and potassium with real-time response. TRELIBS will extend the capabilities of this form of emission spectroscopy to both better sensitivity and higher pressure environments. The difficult problem of quantification is being investigated.

APPENDIX A

The laser was a Quanta-Ray Nd:YAG unit running on the fundamental 1.06 μm wavelength. The pulse length was 80 ns, and the output was 1.0 J (for the coal studies). This resulted in a focused power density in the range 10^8-10^9 W/cm^2, well above the required threshold for breakdown.

The light-gathering lens was only used for the high-resolution work, in which the spectrometer was a 1/2-m instrument with a 1200-line grating. With this spectrometer, only film was used for detection. This level of resolution was required to resolve the sodium D-line doublet, and was also used in a general search for molecular lines and faint atomic lines. The range of the film extended farther into the uv than the diode array. The film results were the basis for the reported species listed in Table I.

Two configurations of 1/4-m spectrometer were used, both with the diode array detection. This was a 1024-element silicon diode array, followed by a Tracor-Northern multichannel analyzer and processor. Hard copies of the data were made on a x-y recorder. Survey spectra, such as Fig. 2, were taken with a 150-line grating and covered the entire wavelength range visible to the diodes. For more detailed spectra, as in Figs. 3 and 4, a 600-line grating was used in the same 1/4-m instrument. With a 50-μm slit about 25 cm from the breakdown, only about 10^{-6} of the emitted light was collected for these data.

APPENDIX B

The BYU gasifier experiments were carried out in a Los Alamos-designed optical test section[2] which was preceded in the flow stream by a cyclone particle separator. The particle density measured in the test section was 1.3 $\times 10^5$ particles/cm^3; the particle size distribution peaked at 20 μm diameter. At this particle density the product stream was opaque, requiring that the breakdown spot be positioned at the edge nearest the observation window, as shown in Fig. 1.

The lower breakdown threshold of the particles (relative to any gas) also made it difficult to get the laser focal spot far enough into the stream to observe, since the particles caused breakdown to occur in the converging beam well before the focus was reached. The laser had to be turned up to its maximum output (1 J) to get an observable focal region, although with gas only in the cell, the focal spot was well established with about 0.2 J of laser output.

From the mass density of the entrained particles, and the estimated focal volume, the actual mass of the sodium and potassium detected may be calculated in an upper limit. The focal volume in the gas was measured to be 25 $\times 10^{-3} cm^3$, so about 2500 particles were contained in that volume. For 20-μm diameter particles of density 2 g/cm^3, the mass of each particle was 10^{-8} g, and the total mass in the plasma was 25 μg. We shall assume that all of the particles were completely vaporized and contributed to the optical signal. We know from an analysis of the ash[3] that the particles contained 4.5% Na_2O and 0.6% K_2O. We conclude that at most, we detected samples of sodium of 0.8 μg, and potassium masses of 0.1 μg. This was with a very inefficient optical system, so that the detection limits are clearly orders of magnitude lower than these worst-case numbers.

TABLE I

SPECIES DETECTED IN BYU FIELD TESTS

Atomic

Na I, K I, H, O I, O II, C I, C II, C III, Ca I, Ca II, Si I, Mg II

Molecular

CN, N_2, CO, O_2

REFERENCES

1. Y. P. Raizer, Laser-Induced Discharge Phenomena, (Consultants Bureau, New York, 1977).

2. E. O. Ballard, "Purged Window Development for Laser Beam Insertion and Signal Retrieval from Coal Gasification Product Streams," unpublished report, Los Alamos National Laboratory.

3. Coal ash analysis by U. S. Geological Survey.

FIGURE CAPTIONS

Figure 1. A schematic view of the apparatus used in our gasifier field tests. The laser beam (entering from the left) breaks down a sample of the product stream. The light from the plasma is dispersed by a spectrometer and detected by a silicon-diode array coupled to a Tracor Northern optical multichannel analyzer. Film detection was also used with a larger spectrometer.

Figure 2. A low-resolution spectrum from the gasifier, covering the wavelength range detectable with the diode array. The dominant hydrogen line made the breakdown appear pink.

Figure 3. A medium-resolution spectrum from the gasifier, made for the identification of the sodium doublet. This assignment was verified by high-resolution spectra that resolved the doublet and confirmed the proper doublet spacing.

Figure 4. The potassium doublet from the gasifier product stream, resolved and calibrated at medium resolution.

Figure 5. The TRELIBS time development of the oxygen spectrum at 0.6 atm, not corrected for the diode array wavelength response. The relative differences show that at early times, the spectrum is the sum of a large white light component and (singly) ionic lines, while at late times only neutral lines can be seen. This improves the signal-to-noise at late times, as demonstrated by the development of lines from a hydrogen impurity.

Figure 6. An illustration of the improved detectability of sodium with late-time TRELIBS. The air background changes are due to the change from ionized lines to neutrals. The early white light is also gone in the late-time spectrum.

Figure 7. Pressure broadening of the LIBS spectrum of helium at 10 atm, and its elimination in a 10-atm TRELIBS spectrum of 3 μs delay.

Figure 8. A calibration apparatus for producing samples of known concentration in the laser focus. A known solution of the species of interest is aspirated by a nebulizer into a measured flow of carrier gas. This is vaporized in a heated tube and flows into the optical cell, where LIBS or TRELIBS can be carried out in the normal manner.

Figure 9. A representative sodium trace taken with the apparatus of Fig. 8. As the signal-to-noise ratio is about 8, this would suggest that the particular detection system in use at that time could be used to detect 20 pg of sodium in the focal spot.

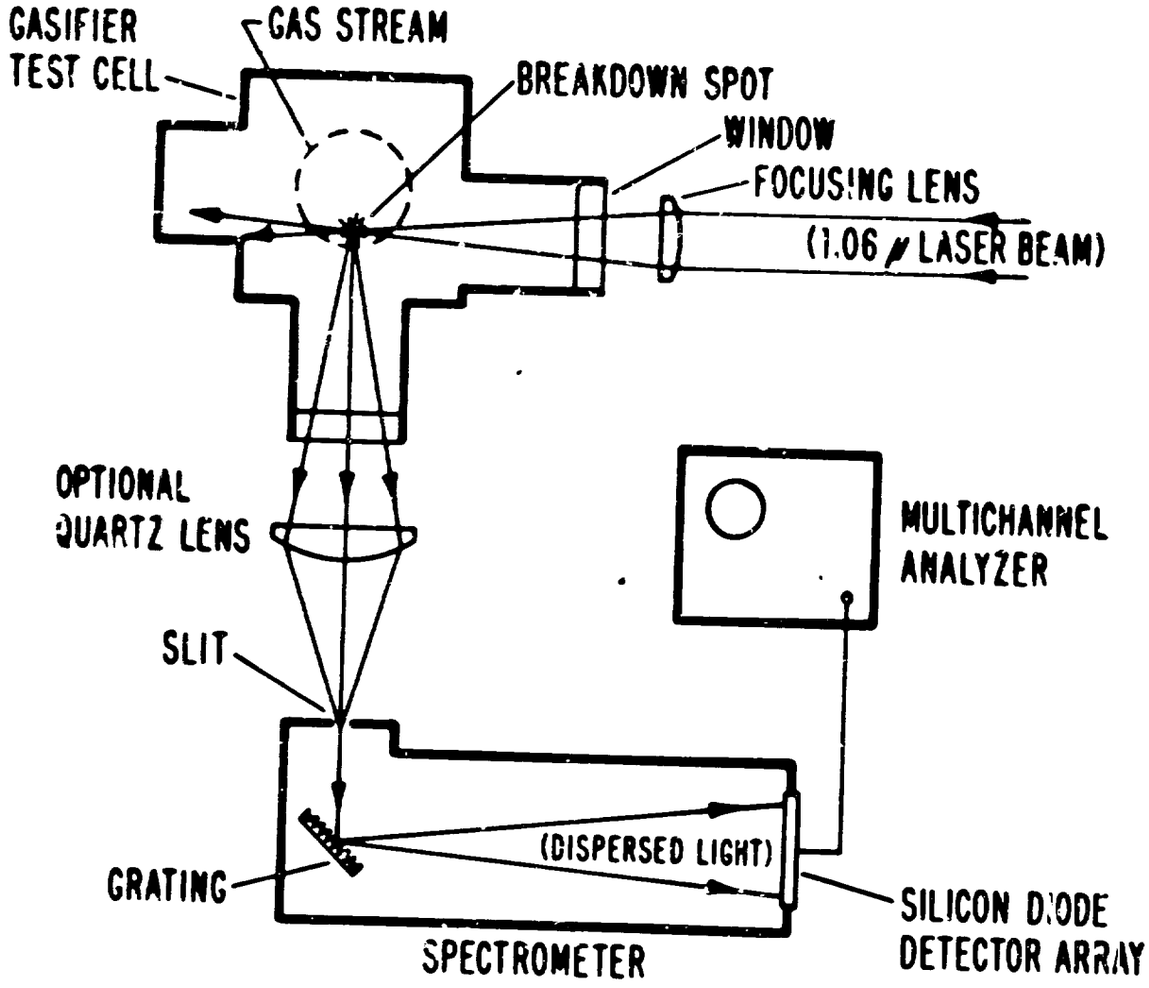

GASIFIER
TEST CELL
GAS STREAM
BREAKDOWN SPOT
WINDOW
FOCUSING LENS
(1.06 μ LASER BEAM)
OPTIONAL
QUARTZ LENS
MULTICHANNEL
ANALYZER
SLIT
(DISPERSED LIGHT)
GRATING
SILICON DIODE
DETECTOR ARRAY
SPECTROMETER

Figure 1

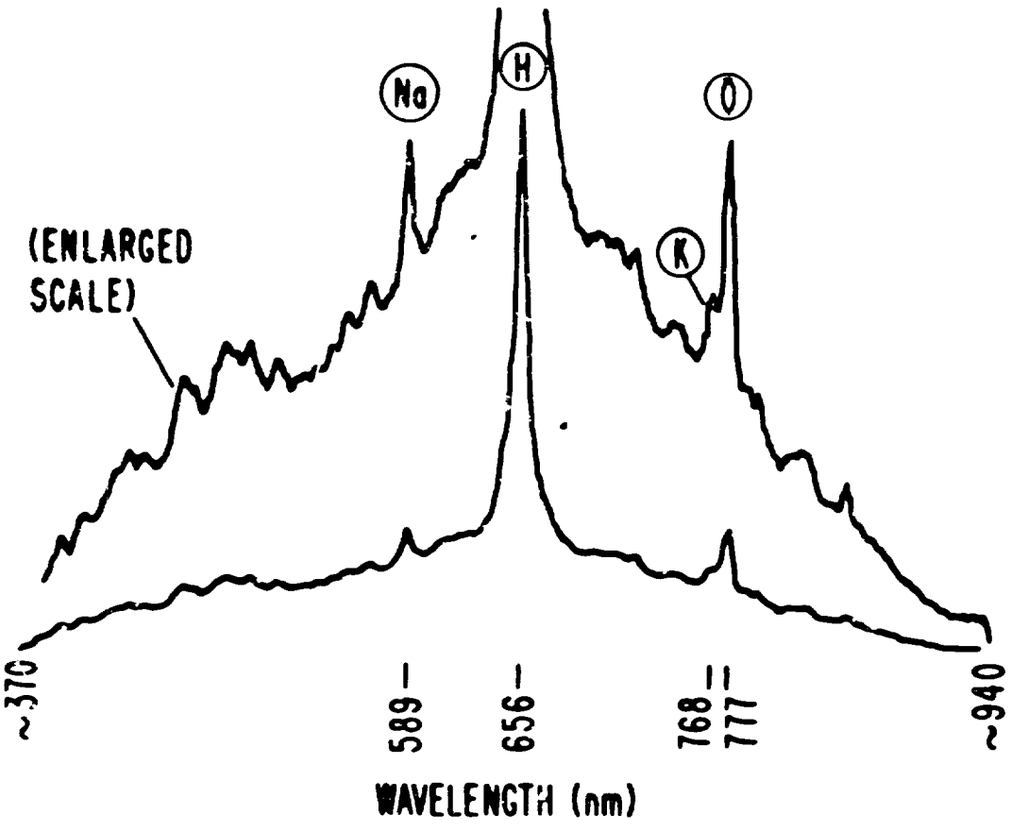


Figure 2

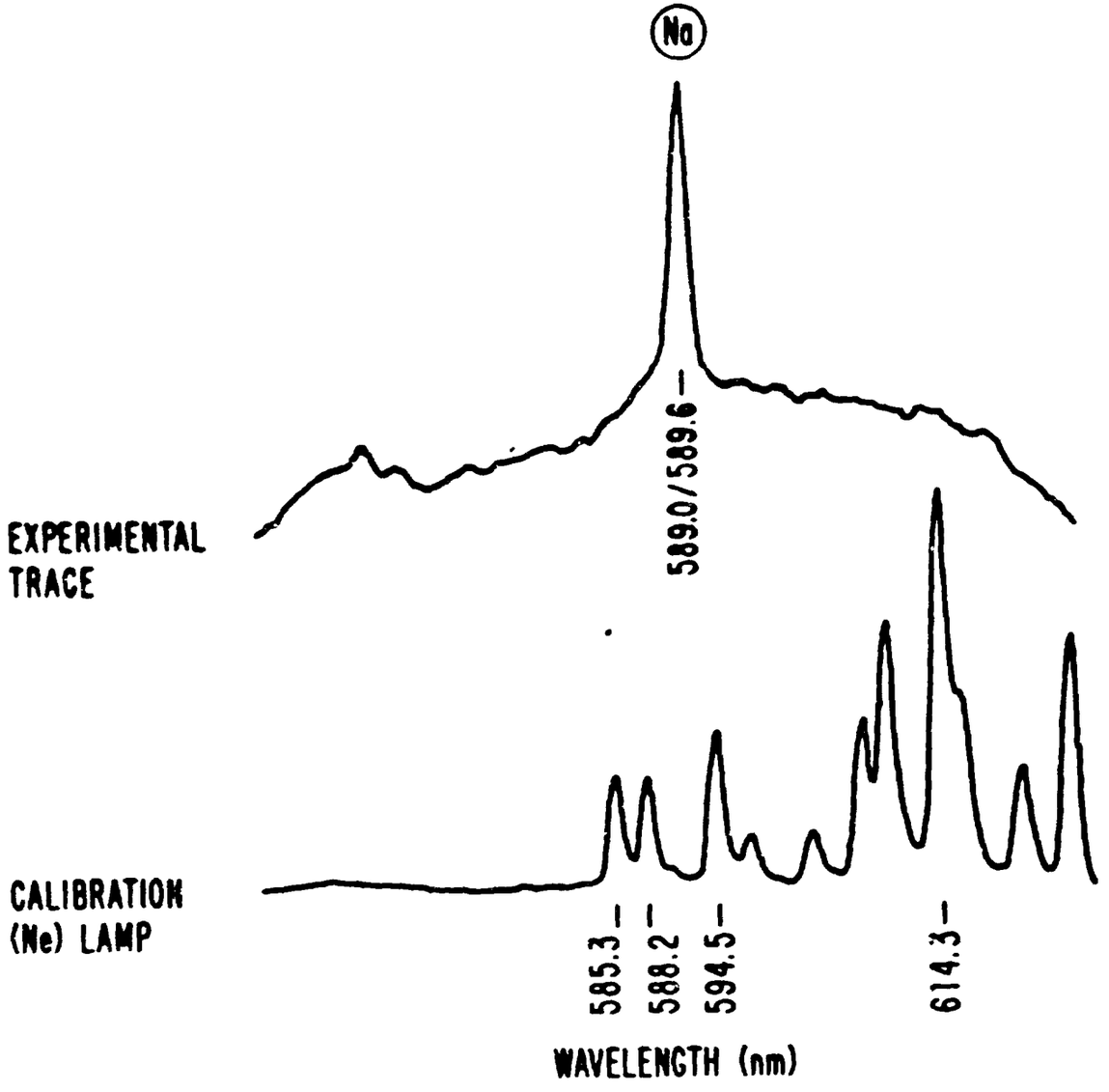

Na
589.0/589.6
EXPERIMENTAL TRACE
CALIBRATION (Ne) LAMP
585.3
588.2
594.5
614.3
WAVELENGTH (nm)

Figure 3

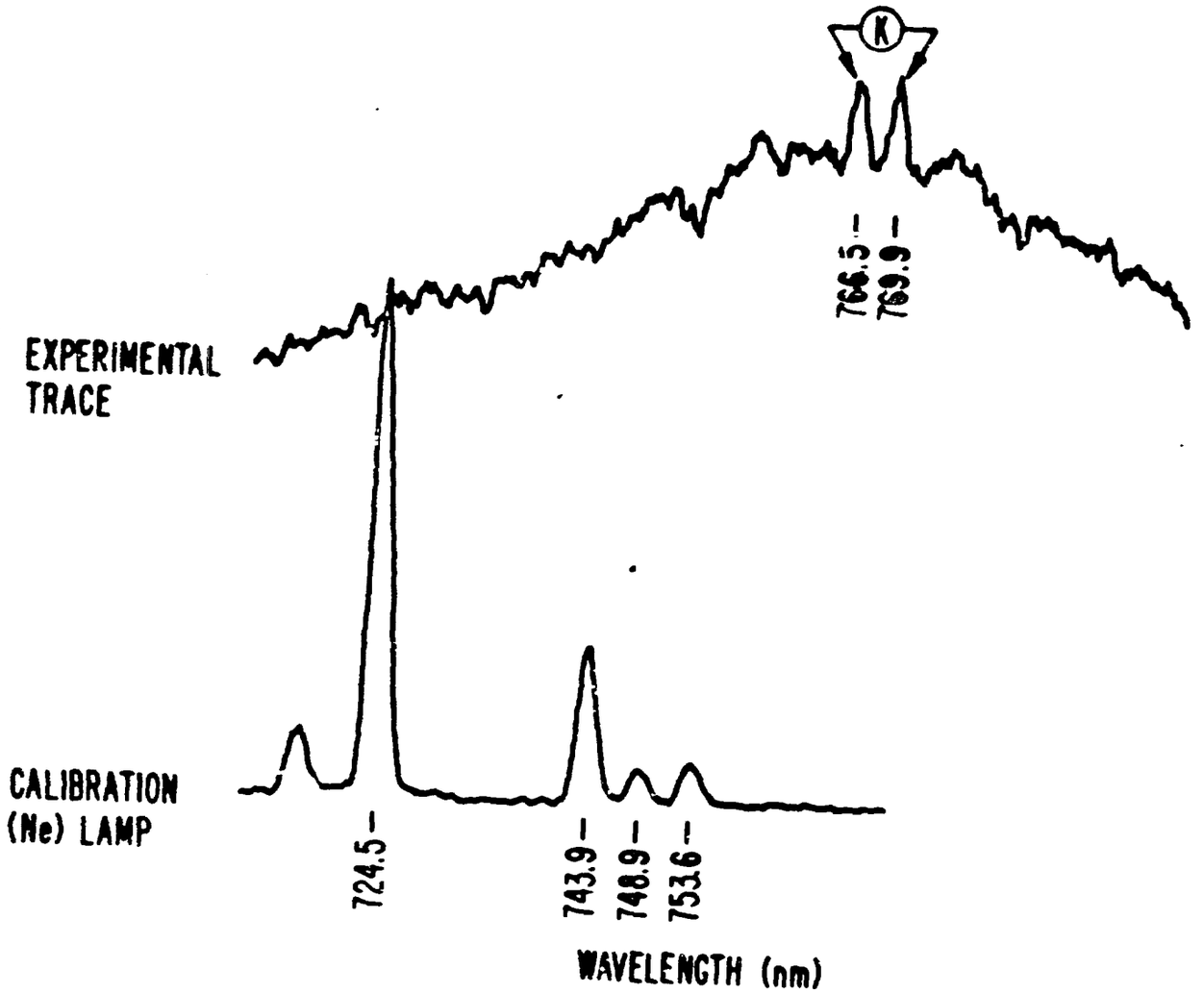

K
766.5
769.9
EXPERIMENTAL TRACE
CALIBRATION (Ne) LAMP
724.5
743.9
748.9
753.6
WAVELENGTH (nm)

Figure 4

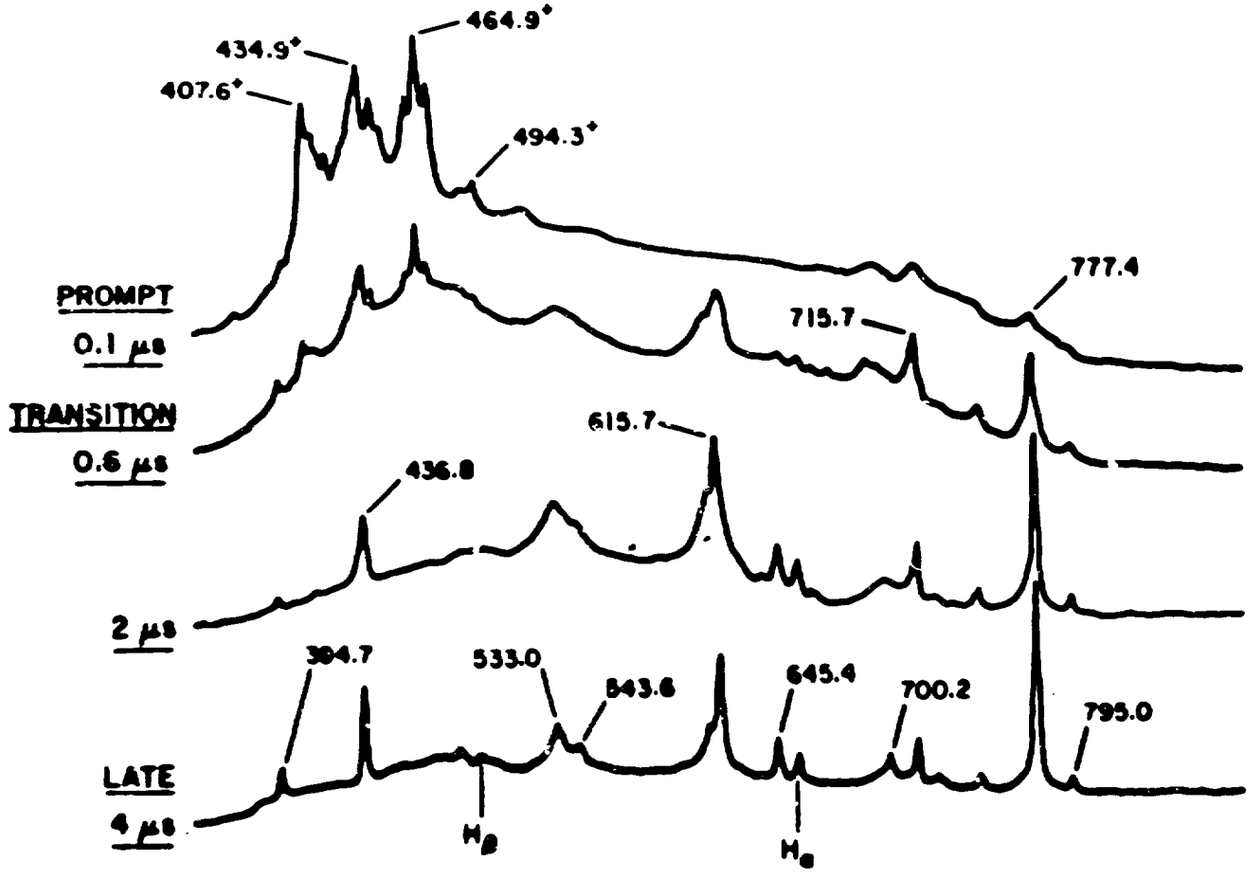

464.9*
434.9*
407.6*
494.3*
777.4
715.7
PROMPT
0.1 μs
TRANSITION
0.6 μs
615.7
436.8
2 μs
384.7
533.0
643.6
645.4
700.2
795.0
LATE
4 μs
Hβ
Hα

Figure 5

TRELIBS OF NaCl in Air

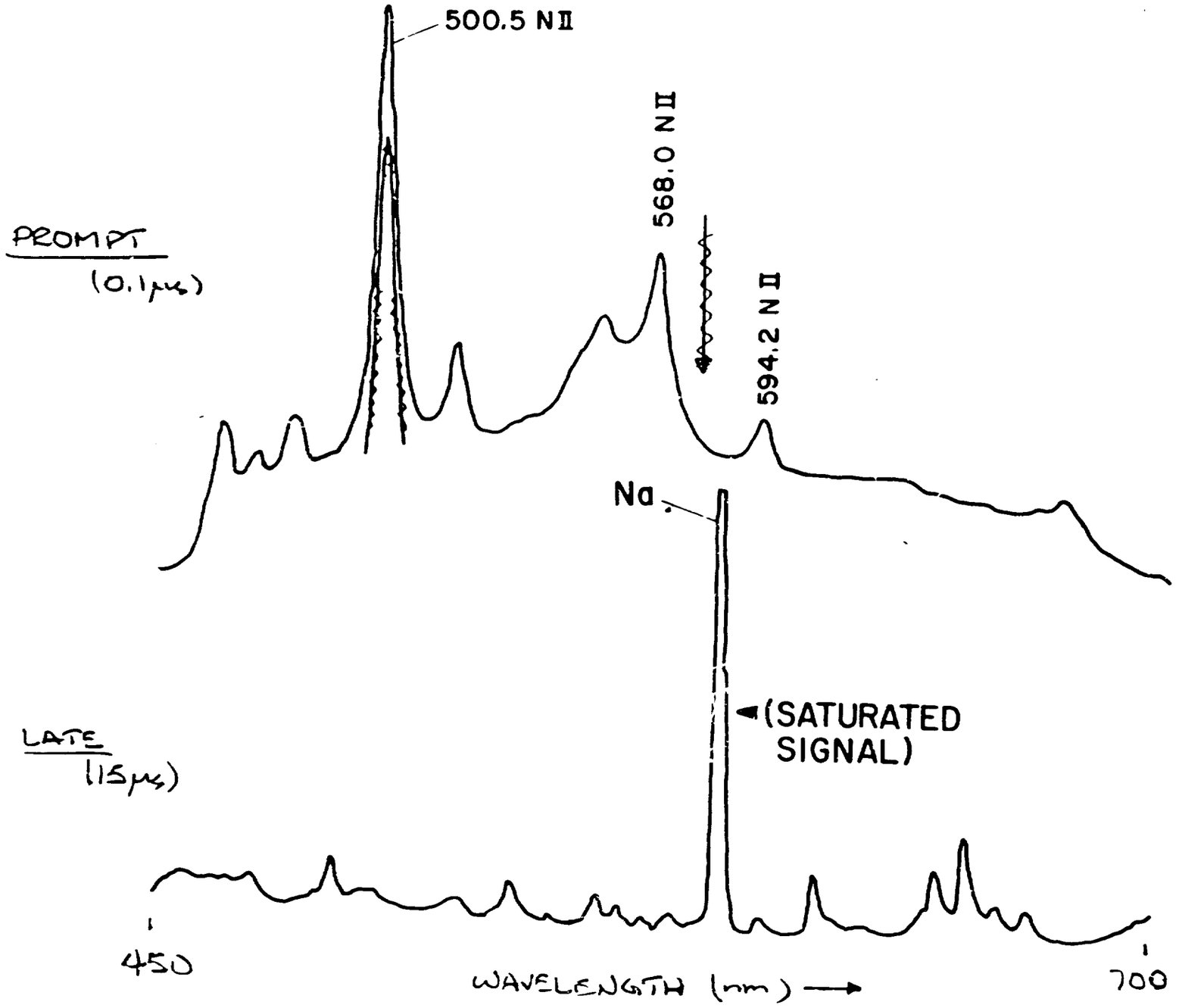


Figure 6

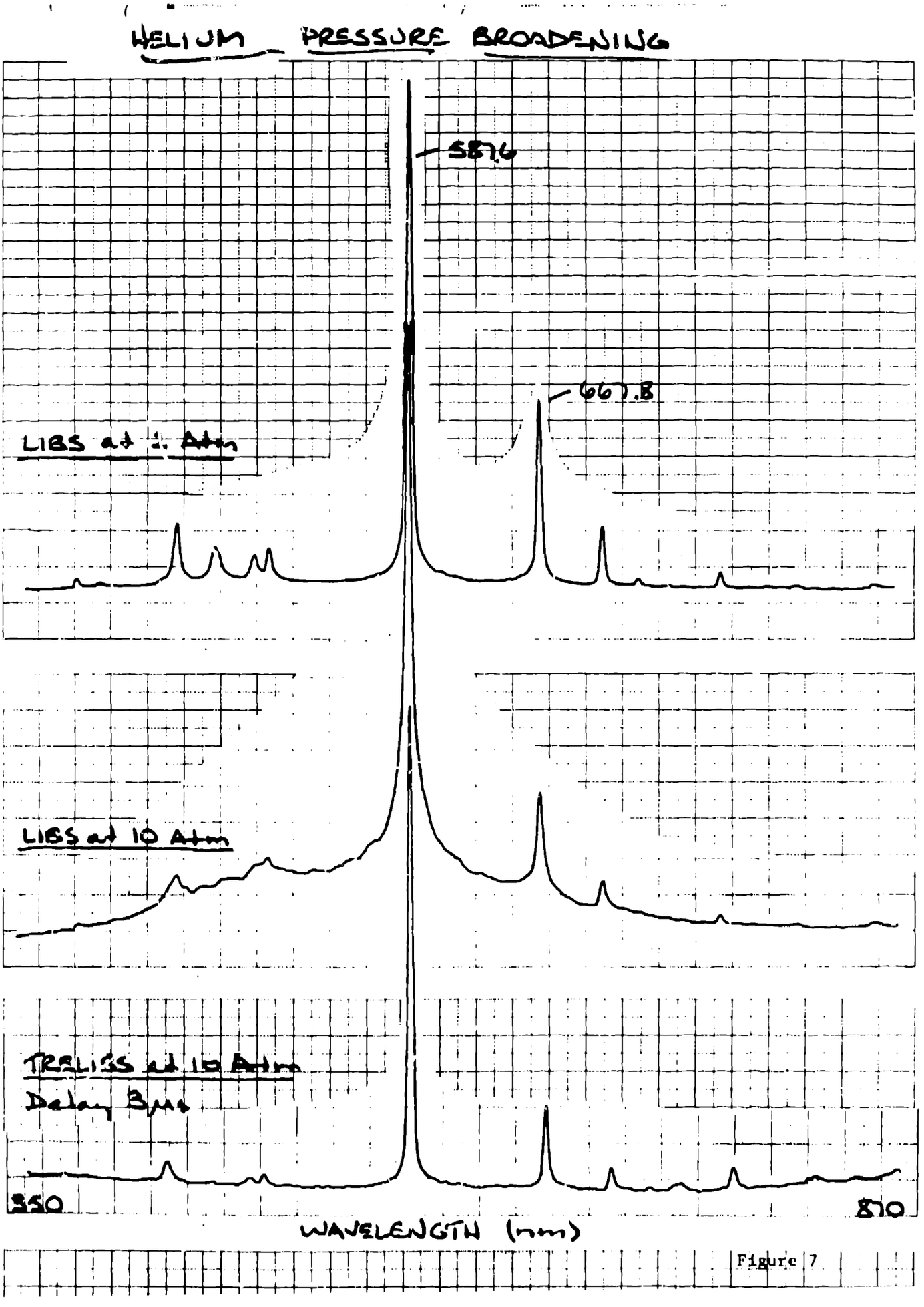

HELIUM PRESSURE BROADENING
587.6
667.8
LIBS at 1 Atm
LIBS at 10 Atm
TRELISS at 10 Atm
Delay 3μs
350
870
WAVELENGTH (nm)

Figure 7

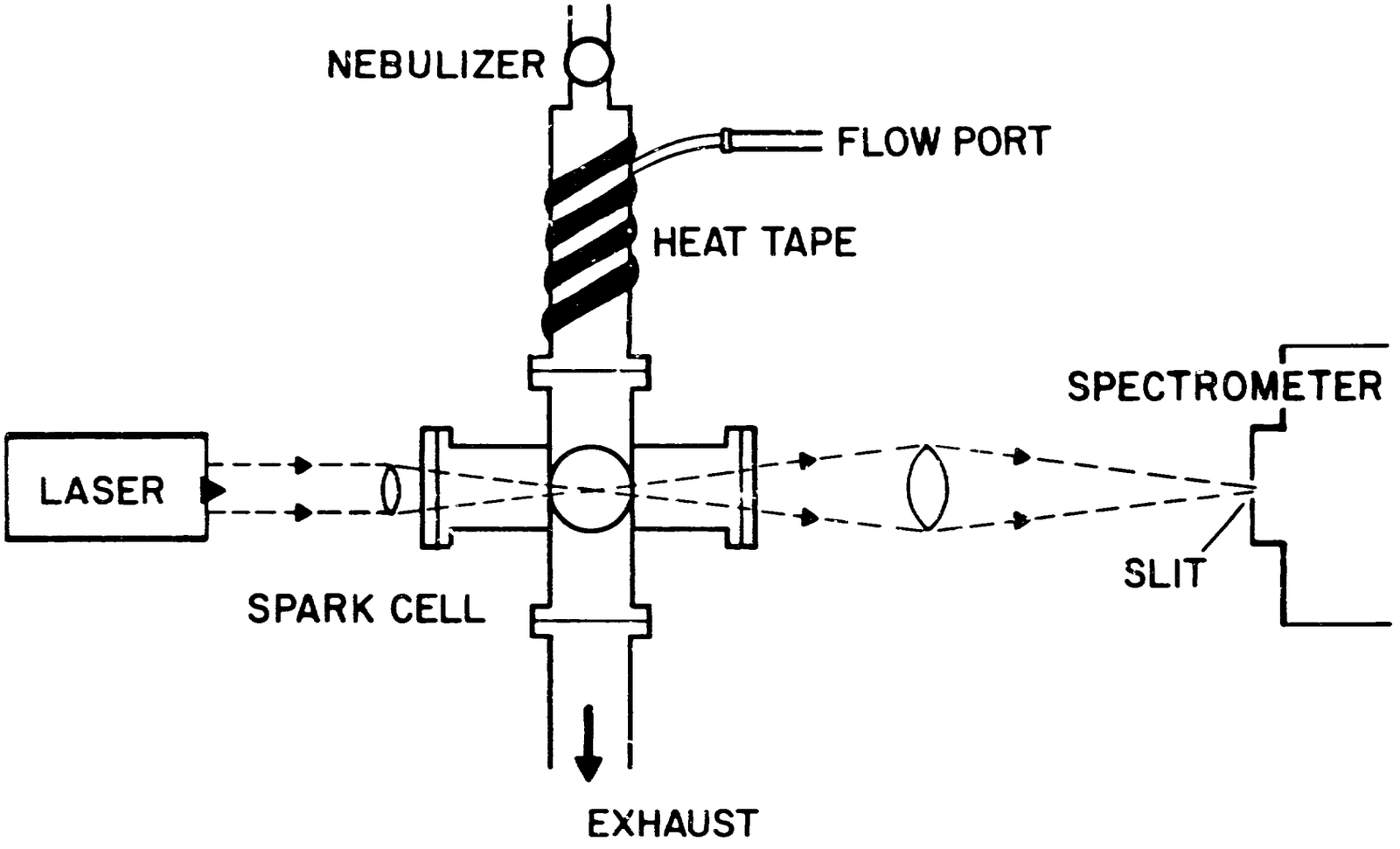

NEBULIZER
FLOW PORT
HEAT TAPE
SPECTROMETER
LASER
SLIT
SPARK CELL
EXHAUST

Figure 8

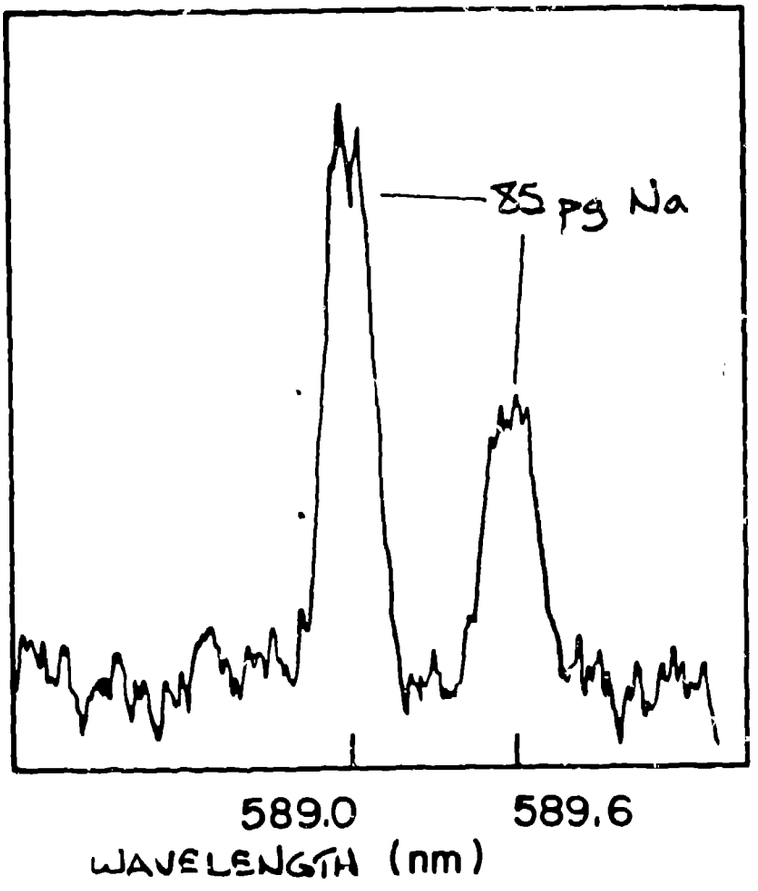
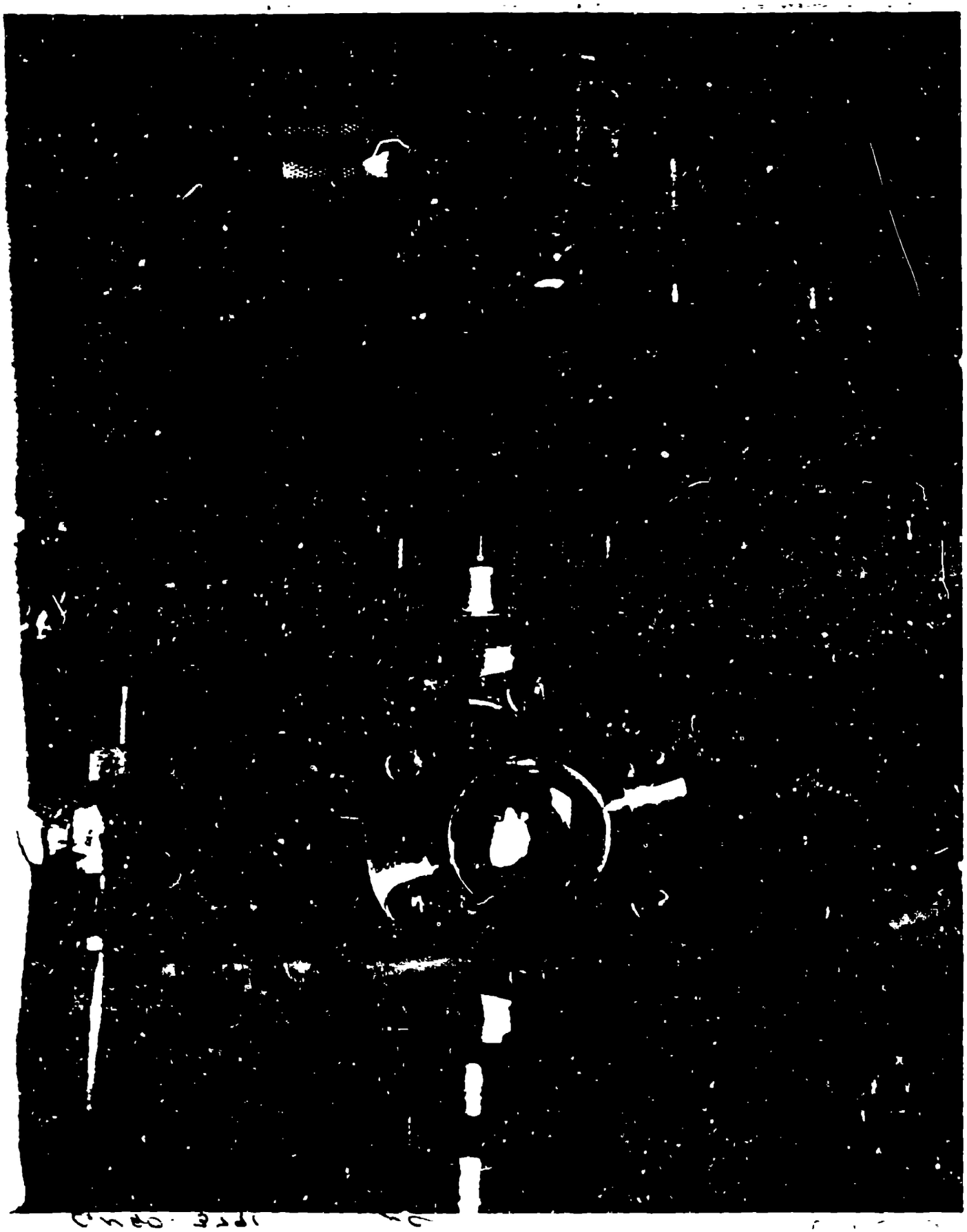
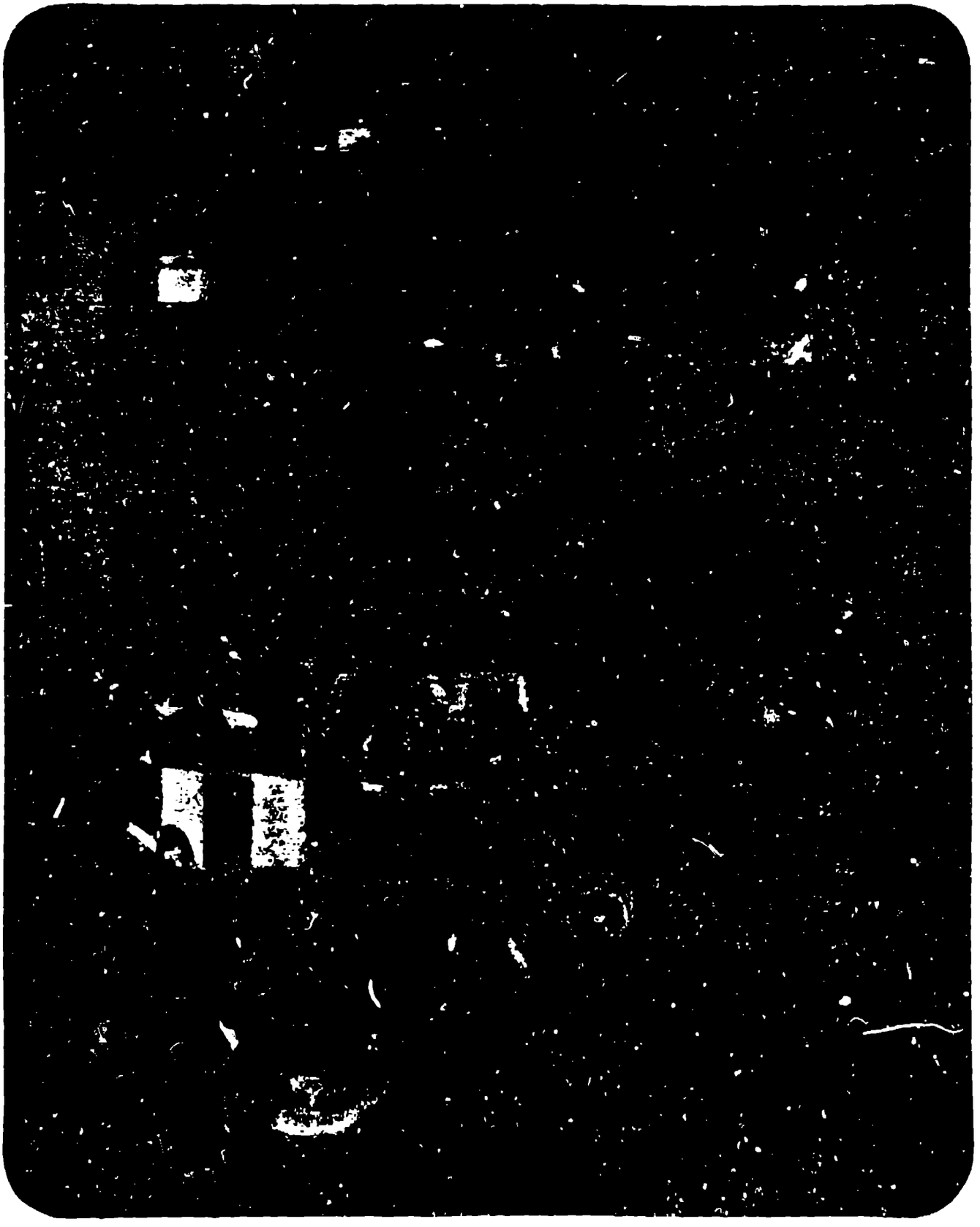


Figure 9

ADDITIONAL VIEWGRAPHS FOR THE ORAL VERSION





U. S. GEOLOGICAL SURVEY COAL ASH ANALYSES[1]

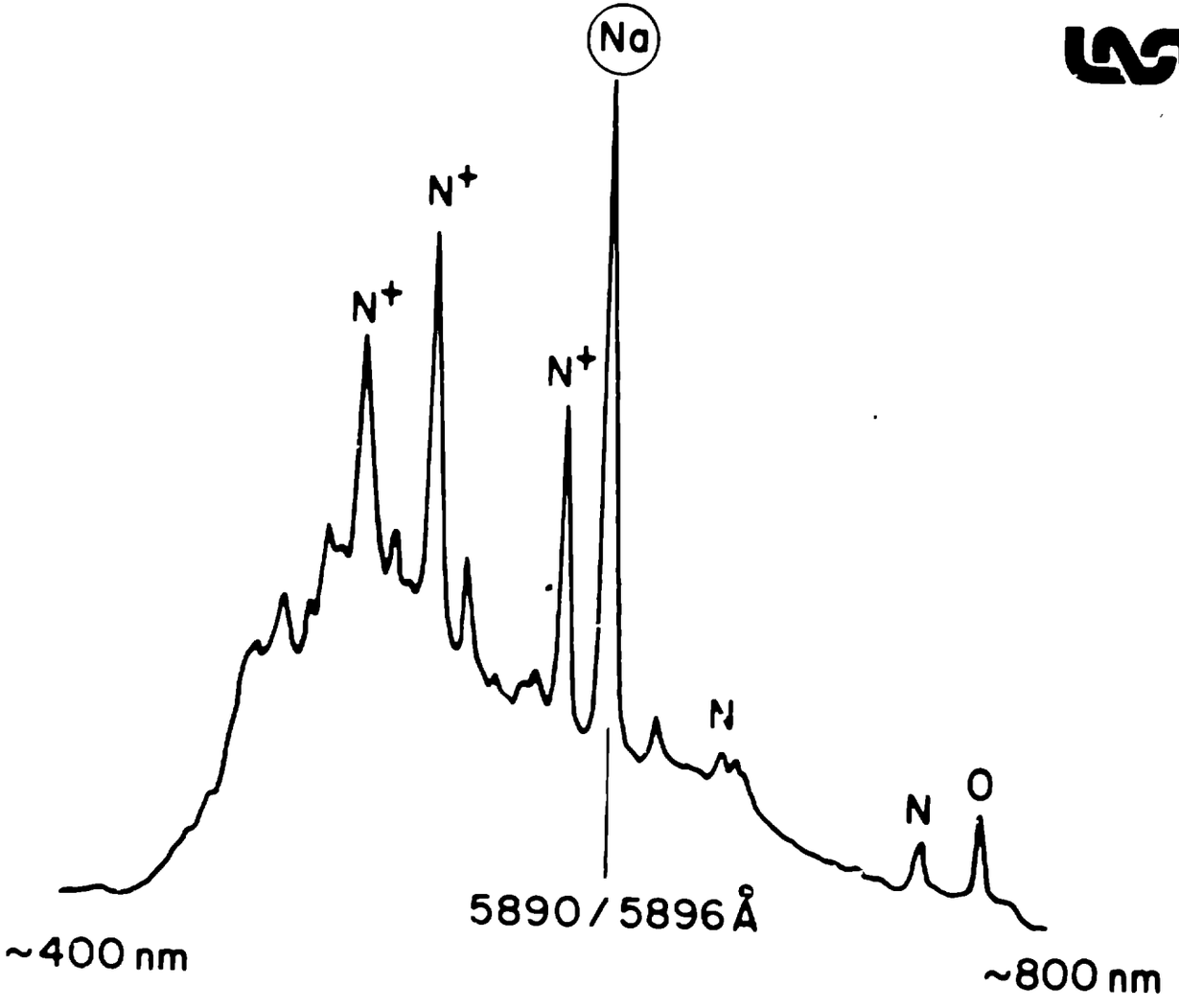
(HIGH VOLATILE B UTAH BITUMINOUS COAL)

	BARREL 2	BARREL 6	BARREL 15	BARREL 23	BARREL 29
MgO	1.08	1.12	0.98	0.94	1.03
Na_2O	4.30	4.48	4.58	4.90	4.48
Al_2O_3	17.0	16.0	19.0	18.0	18.0
SO_3	3.5	4.2	3.5	4.1	4.1
Cl	< 0.20	<0.20	<0.20	<0.20	<0.20
CaO	6.5	6.8	8.2	8.1	7.1
SiO_2	48.0	48.0	43.0	44.0	47.0
P_2C_5	<1.0	<1.0	1.0	<1.0	<1.0
TiO_2	0.89	0.88	0.98	0.96	0.93
MnO	<0.05	<0.05	<0.05	<0.05	<0.05
Fe_2O_3	3.8	3.9	4.2	4.2	3.9
K_2O	0.70	0.71	0.43	0.43	0.65

(1)REPORTED AS PERCENT ASH

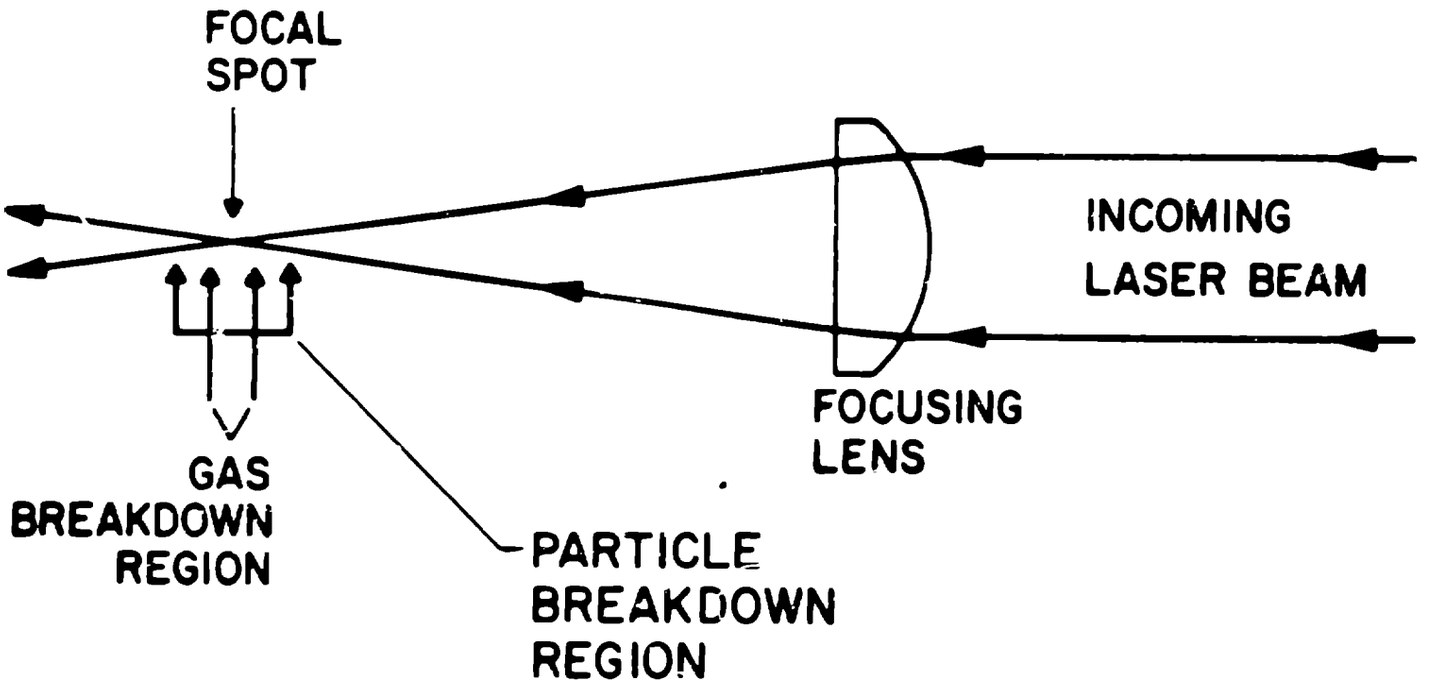
AP-VG-6233

NaCℓ IN AIR



AP-I-VG-6246

LASER-INDUCED BREAKDOWN



AP-1-VG-6227

ROUGH MASS CALCULATION

FOCAL VOLUME:

MEASURED 8 mm x 2 mm

$V \cong 25 \times 10^{-3}$ cc

PARTICLE DENSITY:

MEASURED AVERAGE 1.3×10^5/cc

ESTIMATED AT EDGE: $\rho \cong 10^5$/cc

$\neq$ IN FOCAL VOLUME: $N = V \cdot \rho \cong 2500$

(ASSUME ALL VAPORIZED)

MASS: PARTICLE SIZE $r = 20\ \mu$

ASSUMED DENSITY = 2

V (PARTICLE) = $4 \times 10^{-9}\ \mu$

MASS (PARTICLE) $\cong 10^{-8}$ g

TOTAL MASS = 2.5×10^{-6} g = 25 μg

Na_2O (4.5%) = 1.1 μg

Na (75%) = 0.8 μg

K_2O (0.6%) = 150 ng

K (83%) = 120 ng

BYU TEST DATA: DETECTED SPECIES

(PRELIMINARY RESULTS)

ATOMIC

Na°

K°

H°

O°, O^{+}

C°, C^{+}, C^{2+}

Ca°, Ca^{+}

Si°

Mg^{+}

MOLECULAR

CN

N_2

CO

O_2